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A Hydronium Solvate Ionic Liquid: Facile Synthesis of Air-Stable Ionic Liquid with Strong Brønsted Acidity

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A new kind of ionic liquid (IL) with strong Brønsted acidity, i.e., a hydronium (H_3O^+) solvate ionic liquid, is reported. The IL can be described as $[H_3O^+ \cdot 18C6]Tf_2N$, where water exists as the H_3O^+ ion solvated by 18-crown-6-ether (18C6), of which the counter anion is bis(trifluoromethylsulfonyl)amide (Tf_2N^-; Tf = CF_3SO_2). The hydrophobic Tf_2N^- anion makes $[H_3O^+ \cdot 18C6]Tf_2N$ stable in air. The Hammett acidity function ($H_0 = -4.4$) of molten $[H_3O^+ \cdot 18C6]Tf_2N$, evaluated using the indicator method, is a new record for ILs and indicates strong aciditiy. The findings regarding this proton-condensed solvate IL are of fundamental interest, and will help in the design of media for new acid-base reactions.
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When two or more kinds of substances are mixed, the properties of the mixture can differ from those of the pure substances. Depending on the interactions between the components, some components undergo ionization, e.g. dissociation, protonation, solvation and complexation, due to the neutralization of Brønsted or Lewis acids and bases. Sometimes, the acid-base mixtures can be categorized as ionic liquids (ILs) with melting points below 100°C, which consist only of cations and anions. ILs are regarded as "the third liquid" and some ILs have fascinating physicochemical properties, such as low volatility, low flammability, high chemical, and thermal stability. Furthermore, ILs have received growing interest due to their various uses as media in chemical, biochemical, and/or electrochemical systems.[1–6]

Common anions of ILs such as BF_4^-, PF_6^-, and $AlCl_4^-$ are produced by neutralization, i.e. the adducts of a Lewis acid (BF_3, PF_5, or $AlCl_3$) and a Lewis base (F^- or Cl^-). Examples of ILs prepared through neutralization include solvate ILs.[7–13] Solvate ILs often consist of equimolar molten mixtures of polyethers (linear or cyclic ones, i.e. glymes or crown ethers) and certain metal salts, where the Lewis acidic metal cations are solvated by equimolar amounts of Lewis basic glymes to give complex cations. Besides, neutralization of Brønsted acids and bases produces so-called protic ILs, which are preferred as acid-catalyzed reaction media due to the presence of an acidic proton.[3–6] Since proton transfer is a common chemical transformation, Brønsted acidic ILs receive research attention especially for acid catalysts, fuel cells, biomass processing, polymerization, CO_2 fixation, etc.[6,14–19] The design of stronger Brønsted acidic ILs and evaluation of the acidity in ILs are important for exploring their possible applications as media for acid-base reactions.

Although protons are often written as H^+, H^+ cannot exist as a bare ion in liquids.[20] In aqueous solutions, "H^+_{aq}" exists as $H^+(H_2O)_n$ with n = 1, 2, 3, ... i.e. H_3O^+, $H_5O_2^+$, $H_7O_3^+$, etc. The simplest form is H_3O^+, commonly called a hydronium ion. In a monohydrate acid ($HA \cdot H_2O$), the protons are not bonded to the anion atoms. Protons generally exist as hydronium ions to form $H_3O^+ \cdot A^-$, where HA = HNO_3, H_2SO_4, $HClO_4$, HTfO (Tf = CF_3SO_2), etc.[21–24] However, there is an exception. In solid, anhydrous HTf_2N, the proton is bonded to the anion nitrogen and two oxygens of a neighboring HTf_2N molecule.[25] Likewise, in the case of monohydrate, the imide superacid HTf_2N remains associated and does not protonate water, as suggested experimentally and theoretically. In the infrared measurements for an H_2O and HTf_2N mixture in CCl_4, strong Fermi resonance for N-H vibrations serves as evidence that HTf_2N remains intact, and from the ab initio calculations, spontaneous proton dissociation was not observed for the HTf_2N molecule with the addition of one H_2O molecule.[26,27] Notably, in a non-fluorinated analogue i.e. $(CH_3SO_2)_2NH \cdot H_2O$ imide monohydrate, the proton remains bonded to the anion nitrogen,[28] although the network may change at elevated temperatures to form H_3O^+ trapped in an anionic cage, as reported for $HClO_4 \cdot H_2O$.[24] Protonation of water using equimolar HTf_2N could occur only if H_3O^+ were solvated by ligands, thereby synthesizing a new series of ionic materials, i.e. hydronium solvate ILs, the active protons of which would show strong acidities in the form of (solvate) IL.

A plausible ligand for complexation of H_3O^+ is a crown ether, 18-crown-6-ether (18C6). 18C6 is a good hydrogen-bonding acceptor that binds H_3O^+ cation selectively due to its cavity size resulting in the formation of an $[H_3O^+ \cdot 18C6]$ complex cation.[29–33] In this paper, we report for the first time that H_3O^+ can be stabilized by the addition of 18C6 to $HTf_2N \cdot H_2O$, forming $[H_3O^+ \cdot 18C6]Tf_2N$ (see Fig. 1a). The successful synthesis of $[H_3O^+ \cdot 18C6]Tf_2N$ clarified

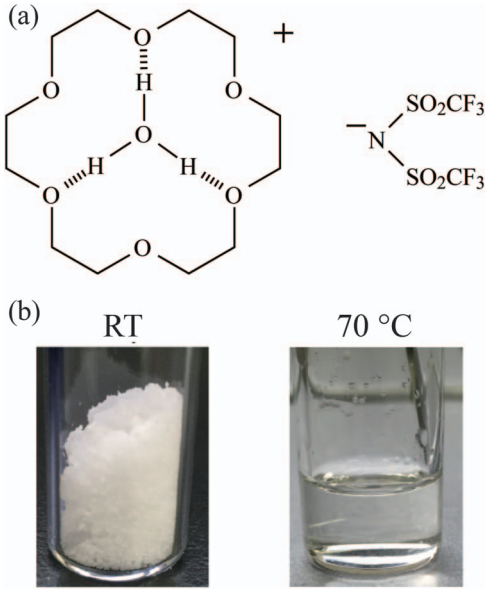

Figure 1. (a) Schematic structure of $[H_3O^+ \cdot 18C6]Tf_2N$ and (b) Photographs of $[H_3O^+ \cdot 18C6]Tf_2N$ at RT and 70°C.

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its unusually low melting point of 68–70°C, compared with the known $[H_3O^+ \cdot 18C6]$ complexes with common anions of ILs, such as ClO_4^-, SbF_6^-, PF_6^-, TfO^-, BF_4^-, $FeCl_4^-$ (110–170°C).[30–33] Moreover, the Tf_2N^- anion is known for its strong hydrophobicity and high chemical stability.[34,35] These characteristic features allowed the facile synthesis of air-stable or non-hygroscopic $[H_3O^+ \cdot 18C6]Tf_2N$ just by vacuum drying of an equimolar 18C6-HTf_2N aqueous solution. We confirm that the hydronium complex $[H_3O^+ \cdot 18C6]Tf_2N$ satisfies the criteria of a solvate IL,[7] containing a negligible amount of neutral molecules. We also reveal that the hydronium solvate IL is highly acidic (Hammett acidity function $H_0 = -4.4$), marking a new record of H_0 among acidic ILs.

Experimental

Materials for $[H_3O^+ \cdot 18C6]Tf_2N$.—18-crown-6 (18C6; Kanto Chemical, 99% purity) and bis(trifluoromethylsulfonyl)imide (HTf_2N; Aldrich, ≥95% purity) were used without further purification. Deionized water was prepared using a Merck Milli-Q Reference A system. *Note*: Wilson et al. have discussed the naming of HTf_2N and Tf_2N^- anion.[36] HTf_2N was originally named as bis((trifluoromethyl)sulfonyl)imide.[37] According to IUPAC nomenclature, HTf_2N is a "sulfonamide", named as 1,1,1-trifluoro-*N*-[(trifluoromethyl)sulfonyl]-methanesulfonamide.[38] Besides, HTf_2N can be viewed as bis(trifluoromethanesulfonyl)amine,[25] but this name ignores one of the accepted principles of nomenclature. However, its conjugate base anion i.e. Tf_2N^- anion is clearly an amide, bis(trifluoromethylsulfonyl)amide or bis(trifluoromethanesulfonyl)amide, commonly abbreviated to TFSA. In some literature, the anion is referred to as an "imide" with the abbreviation TFSI; however, the now-accepted naming is "amide".

Synthesis of $[H_3O^+ \cdot 18C6]Tf_2N$.—18C6 (5 mmol) and HTf_2N (5 mmol) in 5 mL of water were stirred at 500 rpm and heated at 50°C for 1 day in air, followed by vacuum-drying at 50°C for 3 days. A white, non-hygroscopic (air-stable) solid was obtained at room temperature (RT), which melts at ∼70°C, forming a colorless liquid (see Fig. 1b).

Characterization as a solvate IL.—For Raman measurements at RT an integrated Raman system (B&W Tek, innoRam 785), consisting of a semiconductor laser light source (785 nm), an axial transmissive spectrograph, a holographic probe head, and a CCD detector, was used. To lessen the interference by fluorescence, the sample was mixed with active carbon in acetone overnight, then filtered and finally vacuum-dried to obtain a purified sample. The purity was evaluated by chemical analysis. The spectral acquisition time, i.e., exposure time of CCD and the number of exposures was varied for each sample to improve the signal-to-noise ratio of each spectrum. Infrared (IR) measurements were conducted using a JASCO FT/IR–460 plus system. For the IR measurement, Nujol and hexachlorobutadiene mulls painted on a barium fluoride window were used at RT. Nuclear magnetic resonance (NMR) spectra were obtained using a JNM–ECA600 FT NMR spectrometer (JEOL Ltd.). ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were obtained at 75°C. The use of a double NMR tube, purchased from Shigemi Corp. (catalog No. SC-002), prevented mixing of the sample and an external standard: traces of dimethyl sulfoxide-d_6 (Aldrich, 99.9 atom %D) were placed in the outer tube (5.2 mmϕ), and $[H_3O^+ \cdot 18C6]Tf_2N$ in the internal tube (5.0 mmϕ). The melting point of the complex was evaluated by means of a differential scanning calorimeter (DSC; Shimadzu, DSC–60) with a sweeping rate of 5°C min^{-1} by heating from room temperature up to 80°C and then cooling down to 40°C. Thermal gravimetric analysis (TGA) measurements were performed using a Netzsch STA 2500 instrument in a helium atmosphere at 5 K min^{-1}. The 4.9-mg sample was placed on an Al pan and Al_2O_3 was used as a standard.

Viscosity and conductivity.—Conductivity measurements were performed between 75°C and 95°C by the AC impedance method using a Radiometer Analytical CDM230. Viscosity measurements were conducted using Sekonic VM-10A and VM-1G calibrated using a standard solution (Nippon Grease Co., Ltd.). The density of the sample was calculated to be 1.32 g cm^{-3} at 70°C using the measured values of weight and volume.

Electrochemical measurements.—Linear sweep voltammetry (LSV) was conducted in air for $[H_3O^+ \cdot 18C6]Tf_2N$ at 90°C without agitation using a potentiostat (HSV-110, Hokuto Denko). A Pt disk electrode (3 mmϕ, PT-6355, EC Frontier) and a glassy carbon electrode (Toyo Tanso) were used as the working electrode (WE) and counter electrode (CE), respectively. It is reported that a Sn electrode shows stable potential and can be used as the reference electrode (RE).[39] Thus, as the RE a Sn rod was immersed in 50 mmol dm^{-3} $Sn(Tf_2N)_2$—made from SnO and HTf_2N[39]—in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ($EMITf_2N$; Kanto Chemical, 99.9% purity), separated from the main electrolyte by porous Vycor glass. Before the measurements, the WE and CE were washed with acetone and the RE was washed with 1 mol dm^{-3} HCl aqueous solution.

Determination of hammett acidity function.—The Brønsted acidity was evaluated from the determination of the Hammett acidity functions, by an indicator method via UV-visible spectroscopy.[40–42] The Hammett acidity function (H_0) is defined as

$$H_0 = \mathrm{p}K(I)_{\mathrm{aq}} + \log\left([I]_{\mathrm{s}}/\left[I\mathrm{H}^+\right]_{\mathrm{s}}\right) \quad [1]$$

where $\mathrm{p}K(I)_{\mathrm{aq}}$ is the $\mathrm{p}K_{\mathrm{a}}$ value of the spectroscopic indicator referred to in aqueous solution. $[I]_{\mathrm{s}}$ indicates the molar concentration of the unprotonated (I) form of the indicator in the solvent; $[I\mathrm{H}^+]_{\mathrm{s}}$ represents the molar concentration of the protonated ($I\mathrm{H}^+$) forms. 2,4-dinitroaniline (Tokyo Chemical Industry Co., Ltd., ≥99.0% purity, $\mathrm{p}K_{\mathrm{a}}(I)_{\mathrm{aq}} = -4.53$) was used as an indicator. H_0 of $[H_3O^+ \cdot 18C6]Tf_2N$ at 75°C was measured by a UV-visible spectrometer (U-3500, Hitachi). 2,4-dinitroaniline (2.74×10^{-4} mol dm^{-3}) was added and stirred into $[H_3O^+ \cdot 18C6]Tf_2N$ at 75°C to form a solution. The reference absorbance was obtained using 2.74×10^{-4} mol dm^{-3} of 2,4-dinitroaniline in anhydrous ethanol (Wako Chemical).

To compare the acidity between $[H_3O^+ \cdot 18C6]Tf_2N$ and HTf_2N, $[H_3O^+ \cdot 18C6]Tf_2N$ or HTf_2N was dissolved in a common IL, and H_0 was measured at RT. Note that since the use of an IL as a solvent will certainly affect the results, the acidity depends on the selected solvent. In this work, a common IL, $EMITf_2N$, was chosen as the solvent. 2.0×10^{-4} mol dm^{-3} of 2,4-dinitroaniline in $EMITf_2N$ was stirred for 1 day at 110°C in an Ar-filled glove box to remove water. Then $[H_3O^+ \cdot 18C6]Tf_2N$ or HTf_2N was added and stirred in the indicator solution for 10 min at RT in the glove box. These $EMITf_2N$ solutions were placed into screw-capped cells in the glove box, and transferred into a UV-visible spectrometer (U-3500, Hitachi) for measurements at RT. Concentrations of $[H_3O^+ \cdot 18C6]Tf_2N$ ranged from 50 to 2000 mmol dm^{-3}, and those of HTf_2N from 50 to 1000 mmol dm^{-3}.

Results and Discussion

Facile synthesis of $[H_3O^+ \cdot 18C6]Tf_2N$.—The strong hydrophobicity and high chemical stability of the Tf_2N^- anion allowed the facile synthesis of $[H_3O^+ \cdot 18C6]Tf_2N$. Here, water acts bifunctionally, i.e. both as a reactant and as the reaction solvent, from which a solid sample of $[H_3O^+ \cdot 18C6]Tf_2N$ was obtained successfully via vacuum drying at 50°C. In contrast, the known $[H_3O^+ \cdot 18C6]$ complexes have been synthesized using an organic solvent (e.g. tetrahydrofuran, benzene, CH_2Cl_2), into which only a stoichiometric amount of H_2O was added as a reactant with 18C6 and an acid.[30–33] We believe that the reason why an organic solvent was used is that some of the anions (e.g. BF_4^- and $FeCl_4^-$) are hydrophilic and it is difficult to obtain the pure $[H_3O^+ \cdot 18C6]$ complexes. Another reason is that an excess amount of water can cause hydrolysis or decomposition of anions (SbF_6^-, PF_6^-, BF_4^-, $FeCl_4^-$), which creates impurities such as HF or HCl. For

Table I. Result of chemical analysis for $[H_3O^+ \cdot 18C6]Tf_2N$.

element	H [wt%]	C [wt%]	N [wt%]	F [wt%]	S [wt%]
experimental	4.90	29.97	2.40	20.07	11.35
calculated	4.83	29.84	2.49	20.23	11.38

example, it is reported that the PF_6^- anion can be decomposed by moisture and result in HF, POF_3, etc.[43] In contrast, Tf_2N^- salts are known to be dehydrated without significant decomposition.

Classification of $[H_3O^+ \cdot 18C6]Tf_2N$ into a solvate IL.—According to Mandai et al.,[7] solvate ILs should satisfy all the following criteria(1)–(5):

(1) Form a solvate compound between an ion and a ligand(s) in a certain stoichiometric ratio.
(2) Consist entirely of complex ions (solvates) and their counter ions in the molten state.
(3) Show no physicochemical properties based on both pure ligands and precursor salts under usage conditions.
(4) Have a melting point below 100°C, which satisfies the criterion for typical ILs.
(5) Have a negligible vapor pressure under typical application conditions.

Firstly, chemical analysis data for H, C, N, F, and S were consistent with the suggested formulation $[H_3O^+ \cdot 18C6]Tf_2N$ (within ± 0.2 wt% of the calculated value; see Table I). The H_2O content of the complex was 3.29 wt% analyzed by Karl-Fischer coulometric titration, in good agreement with the calculated value (3.20 wt%). In addition, the H_2O content of the sample, kept in a screw-capped vial (not a septum) in air at RT for 2 weeks, did not vary within the experimental limit. This proved the air-stable nature of $[H_3O^+ \cdot 18C6]Tf_2N$, i.e. water absorption is very slow. Consequently, these quantitative analysis results strongly support that the complex was $18C6{:}H_2O{:}HTf_2N = 1{:}1{:}1$ by mole, satisfying criterion (1).

Secondly, the Raman results shown in Fig. 2 satisfy criteria (2) and (3). This point is also supported by the IR results shown in Fig. 3. The Raman spectrum for molten $[H_3O^+ \cdot 18C6]Tf_2N$ clearly illustrates that any bands attributable to free 18C6 ligand molecules are absent. The appearance of the Raman peak centered at 873 cm^{-1}, the so-called breathing mode, means a change in the COC stretching and CH_2 rocking modes of 18C6 due to the complex formation, as in the case of alkali metal ether complexes.[7–13] In the IR spectra, the COC stretching absorption for pure 18C6 is seen as a broad

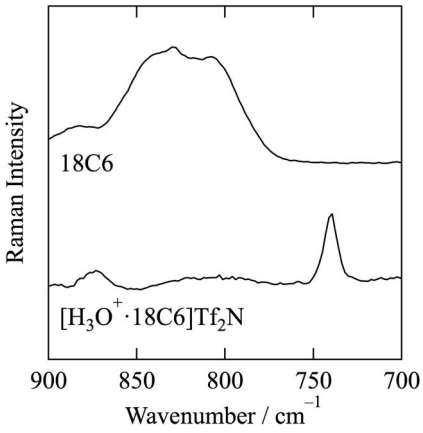

Figure 2. Raman spectra between 700 cm^{-1} and 900 cm^{-1} of pure 18C6 (50°C)[13] and $[H_3O^+ \cdot 18C6]Tf_2N$ (75°C), both in the molten state.

band at 1125 cm^{-1}, which disappeared and split into sharp bands at 1138 cm^{-1} and 1091 cm^{-1} because of $[H_3O^+ \cdot 18C6]$ formation (see Fig. 3a).[30] The presence of H_3O^+ with 18C6 is readily established from the characteristic bands in the IR spectra i.e. ν_1–ν_4 (see Fig. 3b).[30,31] The ν_1 and ν_3 stretching modes give a very broad band centered at 2920 cm^{-1}, which overlaps the sharper maximum at 2880 cm^{-1} arising from the C–H stretching motions of 18C6. The ν_4 band at 1650 cm^{-1} is attributable to the bending mode, and that at 2200 cm^{-1} is the first harmonic of ν_2, i.e. the symmetric bending mode. The ν_2 band at 1100 cm^{-1} is not clearly observed, where a strong band from 18C6 overlaps. Consequently, the IR spectra clearly display the presence of H_3O^+. Therefore, it is proved that all 18C6 ligands coordinate to hydronium cations to form $[H_3O^+ \cdot 18C6]$. The anionic band appears at 739 cm^{-1} without shoulder peaks. Although the resolution is low, its full width at half maximum (FWHM) is comparable to that of the anionic band for "free" Tf_2N^- in our previous report.[44] This indicates that the Tf_2N^- anions are "free" and not forming complex anions such as $[H(Tf_2N)_2]^-$.[45]

Thirdly, DSC measurements revealed a single endothermic peak and a corresponding exothermic peak (see Fig. 4). The ratio of integrated peak areas for the melting and those for subsequent crystallization was close to unity. The melting point was 68–70°C, satisfying criterion (4). Since no additional peaks were seen around the melting points of pure 18C6 (39–40°C) and pure HTf_2N (52–56°C), neither

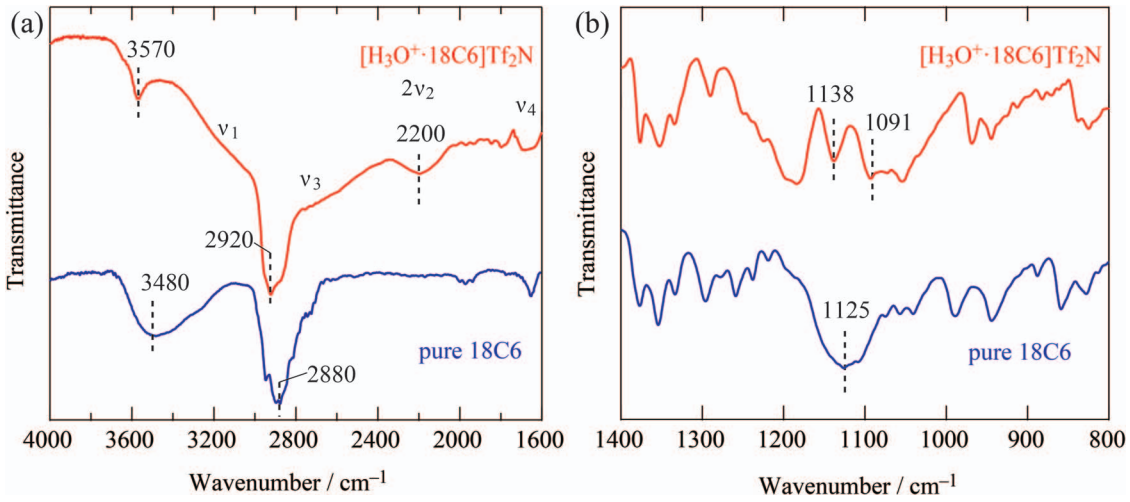

Figure 3. IR spectra of $[H_3O^+ \cdot 18C6]Tf_2N$ and pure 18C6: (a) high-wavenumber region from 1600 cm^{-1} to 4000 cm^{-1} and (b) low-wavenumber region from 800 cm^{-1} to 1600 cm^{-1}.

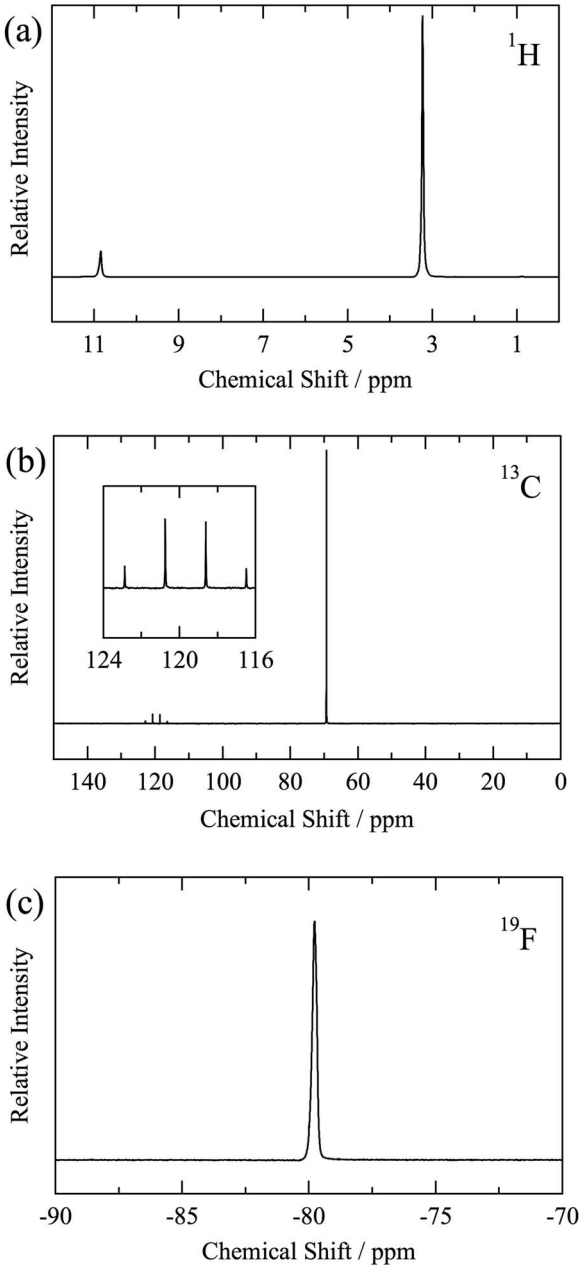

Figure 4. (a) ^{1}H NMR, (b) ^{13}C NMR, and (c) ^{19}F NMR spectra of $[H_3O^+ \cdot 18C6]Tf_2N$ at 75°C.

free ligands nor precursor HTf_2N were included in the sample. This satisfies criterion (3).

Fourthly, the ^{1}H NMR spectra for the molten state (75°C, Fig. 5a) show only two singlets at 10.85 ppm and 3.23 ppm. The former is for H_3O^+ and the latter is for CH_2 of 18C6. The peak area ratio was 1:8, in good agreement with the theoretical ^{1}H ratio for H_3O^+ and 18C6, i.e. $C_{12}H_{24}O_6$. These chemical shifts agree with those for $[H_3O^+ \cdot 18C6]$ salts dissolved in an organic solvent.[32] ^{13}C NMR (shown in Fig. 5b) also revealed the presence of 18C6 ligands and Tf_2N^- anions with an equimolar ratio: a singlet for 18C6 at 69.37 ppm and a quartet for CF_3 of Tf_2N^- (122.89 ppm, 120.76 ppm, 118.62 ppm, 116.50 ppm) with a peak area ratio of 6:1, which agrees the theoretical ^{13}C ratio 18C6:Tf_2N^- = $C_{12}H_{24}O_6$:$N(SO_2CF_3)_2$ = 12:2. In comparison, the NMR results for pure 18C6 at molten state (60°C) showed a distinguishable change in chemical shift (3.26 ppm for H, 70.43 ppm for C; not shown). Fig. 5c displays ^{19}F NMR which exhibits a singlet at

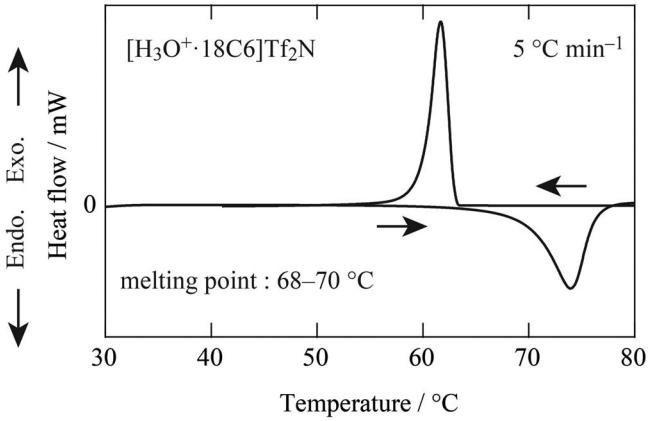

Figure 5. DSC curves for $[H_3O^+ \cdot 18C6]Tf_2N$.

−79.79 ppm, the region characteristic of ionic CF_3SO_2 derivatives: they fall between −71 ppm and −80 ppm ($CFCl_3$), shifting to a higher field as the charge on the CF_3SO_2 group increases.[37] Consequently, the $[H_3O^+ \cdot 18C6]$ complex is the only component cation and Tf_2N^- is the only component anion in molten $[H_3O^+ \cdot 18C6]Tf_2N$. These NMR results satisfy criteria (1)–(4).

Finally, in the TGA data obtained at 5 K min^{-1} no mass loss was detected below 100°C (see Fig. 6). This indicates that neither free 18C6, H_2O nor precursor HTf_2N were included in the sample, satisfying criterion (3). Moreover, a 5 wt% loss was detected at 132°C, a temperature 60°C higher than its melting point. The TGA results suggest a low vapor pressure of $[H_3O^+ \cdot 18C6]Tf_2N$ at around its melting point, that is, $[H_3O^+ \cdot 18C6]Tf_2N$ has a limited window of usage, e.g. between 50–75°C. At such a temperature range, however, the vapor pressure can be negligible, satisfying criterion (5).

In all, criteria (1)–(5) were satisfied to classify $[H_3O^+ \cdot 18C6]Tf_2N$ as a solvate IL. The solvate ILs reported so far are binary mixtures of alkali-metal salts and polyethers.[7–13] In contrast, the hydronium solvate IL, the first example of a nonmetal-cation-solvate IL, is a ternary mixture of water, crown ether, and fluorinated imide superacid. Surveying the analogous compounds would give hydronium solvate ILs that have wide temperature windows of usage.

Conductivity and viscosity of the hydronium solvate IL $[H_3O^+ \cdot 18C6]Tf_2N$.—It is interesting to study the bath properties of molten $[H_3O^+ \cdot 18C6]Tf_2N$, since the observed strong acidity implies high proton conduction. Table II lists the conductivities and viscosities at several temperatures. Although the temperature range is narrow, we estimated the activation energy from Arrhenius plots,

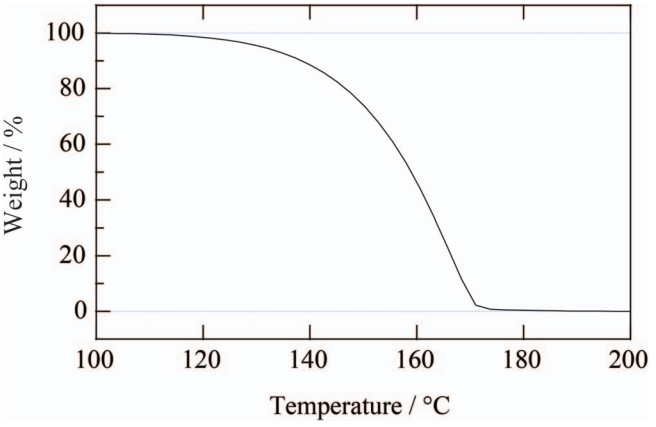

Figure 6. TGA data for $[H_3O^+ \cdot 18C6]Tf_2N$ at 5 K min^{-1}.

Table II. Viscosities and conductivities of molten $[H_3O^+ \cdot 18C6]Tf_2N$.

Temperature [°C]	Viscosity [mPa s]	Conductivity [mS cm^{-1}]
75	42.9	2.36
80	37.0	2.72
85	32.3	3.05
89	29.1	3.43
94	25.5	3.91

giving comparable values: 28.0 kJ mol^{-1} for ionic conduction and 28.9 kJ mol^{-1} for viscous flow with the correlation coefficients $R^2 = 0.999$ in both cases. Figure 7 shows a plot of molar conductivity (Λ_{imp}; measured by AC impedance method) vs. fluidity (η^{-1}), i.e. the Walden plot of $[H_3O^+ \cdot 18C6]Tf_2N$. Here Λ_{ideal} is assumed to be the ideal molar conductivity at a given fluidity of an ideal KCl aqueous solution, where the K^+ and Cl^- ions are completely dissociated and act in an independent fashion. In other words, the absolute value of Λ_{ideal} (S cm^2 mol^{-1}) is equal to that of fluidity, η^{-1} (Poise^{-1} or 10 Pa^{-1} s^{-1}), giving the ideal KCl line (solid line in Fig. 7). The ionicity i.e. the degree of cation-anion dissociation, is estimated as a conductivity ratio $\Lambda_{imp}/\Lambda_{ideal}$: in the Walden plot the measure of ionicity is the vertical deviation from the ideal line $\Delta W = \log(\Lambda_{imp}/\Lambda_{ideal})$.[46] The value of ΔW for $[H_3O^+ \cdot 18C6]Tf_2N$ is -0.36, resulting in $\Lambda_{imp}/\Lambda_{ideal} = 0.44$ ($10^{-0.36} = 0.44$); this represents the situation where the IL is exhibiting as high as 44% of the conductivity that might be expected on the basis of its viscosity. Using ionicity, solvate ILs have been categorized as good ILs ($0 > \Delta W > -1$) and poor ILs ($-1 > \Delta W$):[7–9,13] thus, the hydronium solvate IL is a good IL, and is comparable to common ILs.

We stress that the conductivity of the $[H_3O^+ \cdot 18C6]Tf_2N$ sample is not assisted by excess water, which would help proton conduction. The IR spectra clearly show the absence of unprotonated water in the sample. The broad band due to unprotonated water was observed at 3480 cm^{-1} for pure (as received) 18C6 (see Fig. 3);[47] the water content was 0.14 wt% analyzed by Karl–Fischer titration. For the "pure" complex, however, the broad band at 3480 cm^{-1} due to unprotonated water disappeared, while a sharp band appeared at 3570 cm^{-1}, which may be due to the presence of H_3O^+. Notably, when excess water was added to $[H_3O^+ \cdot 18C6]Tf_2N$, a broad band appeared at 3200–3600 cm^{-1} (not shown). Therefore, unprotonated water, which would help proton conduction, is excluded in the $[H_3O^+ \cdot 18C6]Tf_2N$ sample, proving that intrinsic conductivity data are obtained.

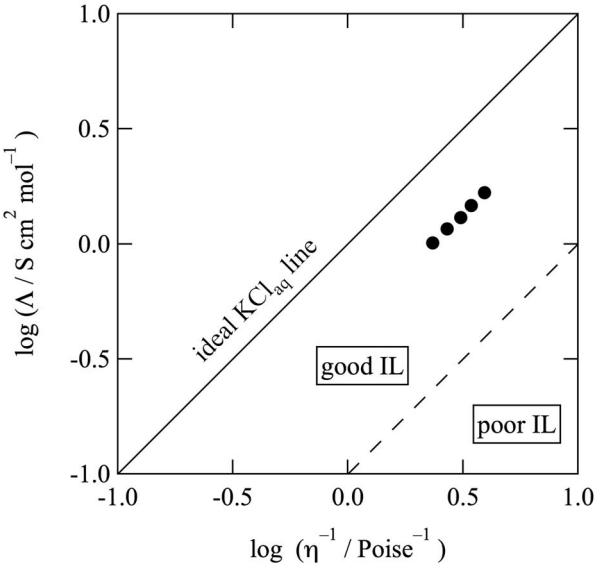

Figure 7. Walden plots for $[H_3O^+ \cdot 18C6]Tf_2N$.

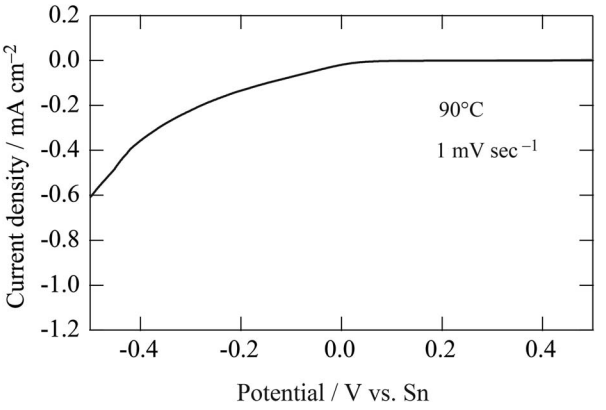

Figure 8. LSV measured for $[H_3O^+ \cdot 18C6]Tf_2N$ with 1 mV sec^{-1} at 90°C.

Acidity of the hydronium solvate IL $[H_3O^+ \cdot 18C6]Tf_2N$.—Figure 8 shows the LSV result for $[H_3O^+ \cdot 18C6]Tf_2N$ obtained at 90°C. An increase in reduction current was observed below approximately +0.026 V vs. Sn where the current reached 20 μA cm^{-2}. Since the redox potential of Sn/Sn^{2+} in aqueous solution is −0.1375 V vs. SHE, the observed reduction potential was not far below 0 V vs. SHE. This strongly suggests high proton activity or high acidic strength of $[H_3O^+ \cdot 18C6]Tf_2N$.

The pH acidity scale cannot be used for ILs because they are non-aqueous. Instead, the Hammett acidity function H_0 of an IL is evaluated from UV-visible measurements of the IL specimen mixed with an indicator.[40–42] By this evaluation method, the ILs with the strongest acidities were reported in 2007 and 2009: $H_0 = -3.6$, both being SO_3H-functionalized ILs.[18,19] Using the indicator 2,4-dinitroaniline with $pK_a = -4.53$, the Hammett acidity function H_0 was determined for $[H_3O^+ \cdot 18C6]Tf_2N$. In Fig. 9, the UV-vis results showed a decrease in the intensity of the peak centered at ∼337.6 nm, indicating that 43% of the indicator was protonated. The value of H_0 was −4.4 for $[H_3O^+ \cdot 18C6]Tf_2N$ at 75°C, stronger than the previous record for acidic ILs ($H_0 = -3.6$).[18,19] The strong acidity in $[H_3O^+ \cdot 18C6]Tf_2N$ results from a combination of the weak bases 18C6 and H_2O and the superacid HTf_2N. In addition, since the amount of free water is negligible, the leveling effect of water is absent in $[H_3O^+ \cdot 18C6]Tf_2N$.

Although $[H_3O^+ \cdot 18C6]Tf_2N$ is a solid at RT, it also showed strong acidity when dissolved into a RT IL. Table III lists the value of H_0 at several concentrations of $[H_3O^+ \cdot 18C6]Tf_2N$ in $EMITf_2N$ solution. The strongest H_0 was −4.6, obtained at 2 mol dm^{-3}. For comparison, H_0 of HTf_2N in $EMITf_2N$ solution was also investigated. Table IV lists

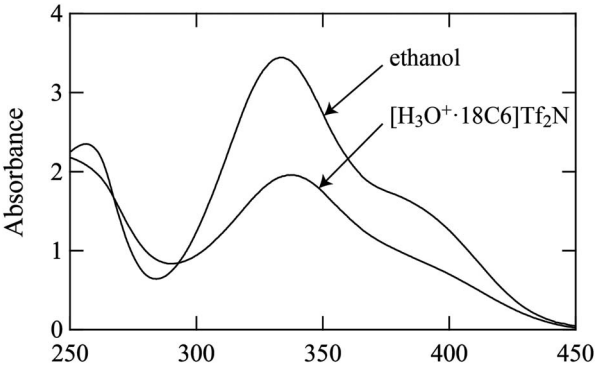

Figure 9. UV-Vis absorption spectra of 2.74 × 10^{-4} mol dm^{-3} 2,4-dinitroaniline in (a) ethanol and (b) $[H_3O^+ \cdot 18C6]Tf_2N$ at 75°C.

Table III. Calculation of the Hammett function for $EMITf_2N$ solution of $[H_3O^+ \cdot 18C6]Tf_2N$.

$[H_3O^+ \cdot 18C6]Tf_2N$ [mmol dm^{-3}]	Abs. $_{max}$	$[I]$ [%]	$[IH^+]$ [%]	H_0
0	3.2	100	0	-
50	2.8	88	12	–3.7
200	2.5	79	21	–4.0
400	2.2	71	29	–4.1
1000	1.8	56	44	–4.4
2000	1.4	45	55	–4.6

Table IV. Calculation of the Hammett function for $EMITf_2N$ solution of HTf_2N.

HTf_2N [mmol dm^{-3}]	Abs.$_{max}$	$[I]$ [%]	$[IH^+]$ [%]	H_0
0	3.2	100	0	-
50	1.6	49	51	–4.5
100	1.2	36	64	–4.8
200	0.7	22	78	–5.1
400	0.5	14	86	–5.3
1000	0.2	6	94	–5.7

the values of H_0 at several concentrations of HTf_2N in $EMITf_2N$ solution, and Fig. 10 displays the H_0 for $[H_3O^+ \cdot 18C6]Tf_2N$-dissolved and HTf_2N-dissolved $EMITf_2N$ solutions. In both cases, a linear relationship was seen between H_0 and the logarithm of concentration. Note that similar H_0 values ($-4.5 < H_0 < -5.5$ for $0.5 < -\log C < 1.0$) have been reported for HTf_2N-dissolved $BMITf_2N$ solution (BMI = 1-butyl-3-methylimidazolium).[42] Consequently, it was revealed that, in $EMITf_2N$ solutions, $[H_3O^+ \cdot 18C6]Tf_2N$ is a weaker acid than HTf_2N, but still a strong acid since the difference in H_0 is just 1 at the same concentration. Since HTf_2N is hygroscopic and sublimes, the air-stable $[H_3O^+ \cdot 18C6]Tf_2N$ is advantageous over HTf_2N in terms of handling.

Conclusions

$[H_3O^+ \cdot 18C6]Tf_2N$ is the first solvate IL, where nonmetal cations are solvated. This hydronium solvate IL shows strong acidity—due to the absence of the leveling effect of unprotonated water—and a good degree of cation-anion dissociation. The facile synthetic process for $[H_3O^+ \cdot 18C6]Tf_2N$ is advantageous over those for other strongly acidic ILs, such as SO_3H-functionalized ILs, which require many laborious steps to obtain the final products. The acidity of hydronium solvate IL can be tuned by using ligands such as thio-crown ethers (more acidic) and aza-crown ethers (more basic). Tailoring the acidity of ILs via facile synthesis is of special interest for many bio- and electro-chemical applications.

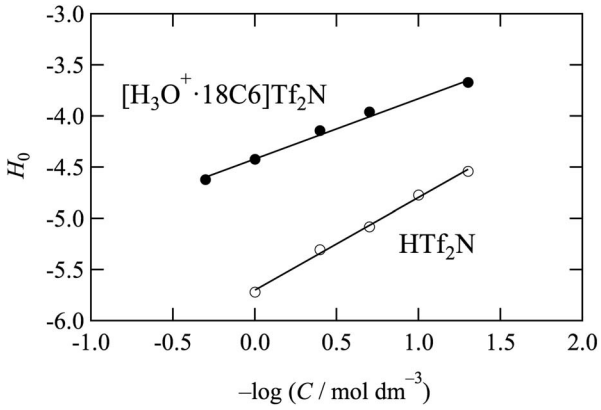

Figure 10. Hammett acidities for $[H_3O^+ \cdot 18C6]Tf_2N$ (closed circles) and HTf_2N (open circles) dissolved in $EMITf_2N$.

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